REFRACTORIES FOR GLASS PRODUCTION

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TRADITIONAL AND NEW REFRACTORY MATERIALS FOR CONSTRUCTION AND REPAIR OF GLASS-MELTING FURNACES

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A wide spectrum of traditional aluminosilicate refractory materials (chamotte, mullite-silica, mullite, mullite-corundum) for the construction and repair of glass-melting furnaces produced at the Borovichskii Refractory Works is considered.

The Borovichskii Refractory Works is well known in various sectors of industry as a producer of aluminosilicate refractories. In 1857, that is, 147 years ago Emmanuel Nobel built in Borovichi the first Russian factory producing "fire-constant bricks from the fire-constant clay found there". The unique properties of kaolins from the Borovichsko-Lyubytinskoe deposit containing up to 45% alumina and the advance of an industrial revolution in Russia encouraged the Swedish industrialist to make this bold step. Throughout its subsequent history the factory carried on its main production based on local materials and also put in production new lines of refractories based on achievements of the scientific and technical progress and taking into account the demand of consumers [1].

At present the Borovichskii Refractory Works is one of the largest Russian factories producing refractories, it is equipped with state-of-the art machinery, has the full production cycle, and, while continuing the traditional refractory products, actively implements the latest scientific developments.

TRADITIONAL REFRACTORIES PRODUCED BY BOROVICHSKII REFRACTORY WORKS

Chamotte refractories used to construct various elements of glass-melting furnaces traditionally enjoy great demand. The advantage of these refractories is their relatively low price, but their low physicochemical parameters restrict their possible application. It should be noted that in repair and especially in constructing new furnaces, customers instead of refractory grades ShA and ShB prefer chamotte refractories with better technical parameters, such as ShN-38 and ShV-42 and in some cases blast furnace refractories ShPD-39 and ShPD-41. In February 2003 the company produced and delivered refractory products ShPD-39 according to the blueprints of the Kavminsteklo JSC that were used to build a lower regenerator structure.

The Borovichskii Refractory Works offers a wide range of mullite-silica, mullite, and mullite-corundum refractories with aluminum oxide content ranging from 45 to 95%, of standard shapes and sizes or made to customer's orders. Refractories MLS-62, MKS-72, and MKV-72 are extensively used to erect the lower structure and walls of regenerators and in some cases for the regenerator checkerwork as well. The physicochemical parameters of aluminosilicate refractories for the construction and repair of glass-melting furnaces are listed in Table 1.

A distinctive characteristic of the Borovichskii Works products is their high quality, The factory specialists have developed a number of measures intended to maintain high quality of the products: the company has it internal quality standards with parameters even stricter than those prescribed by the state standards and technical regulations, double acceptance-check is eliminated. The physicochemical parameters of some products are listed in Table 2.

If necessary, increased requirements are specified in a contract for delivery of refractories and are strictly complied with. For instance, the Borovichskii Works in 2004 supplied refractories for the construction of a tank glass-melting furnace at the Severskii Glass Factory (Tomsk Region) designed by the Czech Company SKLO STROJ. Mullite and mullite-corundum refractories for regenerator walls were produced with mechanical strength no less than 40 – 60 N/mm^2

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TABLE 1

Parameter	Aluminosilicate refractories						
	ShA (GOST 390–96)	ShN-38 (TU 1546-002-00190495–97)	ShPD-39 (GOST 1598–96)	ShV-42 (GOST 20901–75 with modif. 1 – 5)	KMKRU-45 (TU 14-8-647–94)	MLS-62 (GOST 24704–94)	MKV-72 (GOST 20901–75 with modif. 1 – 5)
Mass content, %:							
Al_2O_3, at least	30	38	39	42	45	62	72
Fe_2O_3, not more than	–	–	1.5	1.7	3.5	1.5	1.2
Refractoriness, °C, at least	1690	1730	1750	1750	1730	–	–
Additional linear shrinkage, %, not more than at temperature, °C:							
1400	–	0.4	–	–	0.4	–	–
1450	–	–	0.2	0.4	–	–	–
1500	–	–	–	–	–	0.4	–
1600	–	–	–	–	–	–	0.8
Open porosity, %, not more than	24	21	16	14 – 20	19	24	21 – 24
Compression strength, N/mm^2, at least	20	22	50	30 – 40	30	25	30 – 50
Deformation start temperature under loading, °C, at least	1300	1400	1440	1500	–	1450	1550
Apparent density, g/cm^3, at least	2.0	–	–	–	2.3	2.3	–

(1 N/m^2 = 1 Pa, 1 N/mm^2 = 10 MPa) (depending on the product configuration) and porosity not more than 20 – 21%.

Starting with 1994 the company was the first in the industry to undertake voluntary certification of its products. At present 15 certificates have been received meeting the requirements of the State Standardization Committee of Russia; certified products now constitute over 70% of the total product range. The quality management system at the company has been certified to comply with GOST R ISO 9001–2000 Standard. The products made at the Borovichskii Refractory Works and the company itself were several times decorated with honorary diplomas and prizes at Russian and international exhibitions, including the "1000 best Russian factories" diploma in 2002 and twice "100 best products in Russia" diploma in 2000 and 2002 [2].

In the difficult period of economic reforms the company preserved and even upgraded its mold shop. This makes it possible to produce refractories of complicated configurations, including non-standard products; grinding of products can be performed at the customer's request.

Today the product range of the company counts 34 items and more than 2500 standard sizes.

The Borovichskii Works offers to the customer a wide range of nonmolded refractory materials: lump kaolin, milled chamotte and clay, chamotte fillers, aluminosilicate plasticized marl (MSh-28, MShB, MSh-39, MB-56, MML-62, MMK-72, MMKB-75), high-alumina cement Tsembor-73, dry concrete mixtures, and ramming mixtures (SKBT, SMKBT, SMKRBT, SShBT, SALBT-1.6, SMKN-85, MKN-94).

NEW REFRACTORIES DEVELOPED AT THE BOROVICHSKII REFRACTORY WORKS

High-temperature and refractory heat-insulating materials. The progress of Russian economics is related to solving various engineering problems, namely, substantially decreasing power and heat losses, decreasing material consumption, and ensuring rational and efficient use of all resources. According to the data of the Teploproekt Institute, today the

TABLE 2

Parameter	Simple profile ShA-5		Checkerwork refractories ShN-38-9		High-alumina refractories MLS-62	
	requirements of GOST 390–96	average parameters*	requirements of TU 1546-002-00190495–97	average parameters*	requirements of GOST 24704–94	average parameters*
Mass content of Al_2O_3, %, at least	30.0	38.3	38.0	39.7	62.0	67.9
Refractoriness, °C, at least	1690	1721	1730	1730	–	–
Additional linear shrinkage or growth, %, not more than	–	–	0.4	0.1	0.4	0.2
Open porosity, %, not more than	24.0	21.4	21.0	18.1	24.0	19.7
Compression strength, N/mm^2, at least	20.0	37.4	22.0	47.0	25.0	64.2
Deformation start temperature under loading, °C, at least	1300	1336	1400	1405	1450	1467

* The average values are taken from the product specifications data of the Borovichskii Refractory Works.

TABLE 3

Parameter	Product ShL-1.3	
	requirements of GOST 5040–96	actual values
Apparent density, g/cm^3	Not more than 1.30	1.24
Compression strength, MPa	Not less than 3.5	10.2
Additional linear shrinkage, %, in firing at 1300°C	Not more than 1.0	0.1
Thermal conductivity, W/(m · K), at temperature, °C:		
320 ± 25	Not more than 0.60	0.34
650 ± 25	Not more than 0.70	0.48

average fuel consumption (kilograms of conventional fuel per 1 dollar of product) in Western Europe is 0.5, in USA 0.8, and in Russia 1.4.

The production and rational use of efficient high-temperature heat-insulating materials makes it possible to decrease material consumption in furnaces by decreasing the furnace weight 9 – 11 times and reducing noneffective heat losses into the ambient medium and to reduce the total fuel consumption in continuous furnace 10 – 15 times and in batch-type furnaces by 45% and more [3].

In 1980s the government instructed the Borovichskii Refractory Works to stop the production of lightweight refractories. However, as a consequence of insistent demands of the customers, the company again had to pay its attention to the production of lightweight refractories. In 1994 for replacing imported lightweight refractory products of a specially complicated profile in the pellet-metallizing furnace at the Oskol'skii Electrometallurgical Works the specialists of the central laboratory of the Borovichskii Works developed and patented a technology for producing lightweight chamotte refractories ShL-1.3 by plastic molding using foam polystyrene as the burning-out additive. The use of this additive made it possible to optimize the structure of the products providing for their thermomechanical and heat-insulating properties considerably exceeding the requirements of GOST 5040–96. Materials of such strength can be used in bearing structures of furnaces and in working brickwork layers. The parameters of products ShL-1.3 using foam polystyrene are listed in Table 3.

The Borovichskii Works produces refractories with the specified parameters not only of standard shapes and sizes, but also to customer orders, including plates of size 550 × 450 × 65 mm. In 2004 lightweight chamotte refractories ShL-1.3 were supplied for the construction of glass-melting furnaces at the Chagodoshchenskii Glass Factory and the Belsteklоprom Company (city of Gomel).These refractories were used for the thermal insulation of walls and the bottom of the melting tank.

To decrease the production cost of lightweight refractory, the research center of the company analyzed the production of lightweight refractories with other burning-out additives, i.e., coke powder and sawdust and obtained positive results.

Using the foaming methods, lightweight chamotte refractories of density 0.4, 0.6, and 0.8 g/cm^3 were developed. By combining the burning-out additive and foaming methods, a lightweight corundum material of density 1.1 g/cm^3 was obtained.

A commonly used industrial method for obtaining a porous structure in a material is the introduction of a porous filler. Swelled vermiculite has a set of unique properties: low bulk density (80 – 120 kg/m^3), low thermal conductivity (0.04 – 0.12 W/(m · K)), and relatively high melting temperature (1240 – 1430°C). It is chemically inert, durable, and environmentally safe, which makes it promising for use in high-temperature heat-insulating materials. Heat-insulating materials based on vermiculite have refractoriness below 1580°C, therefore, they are not classified as refractory, but as their service temperature exceeds 1000°C, they are regarded as high-temperature materials.

The developed vermiculite heat-insulating products with a low apparent density (400 – 1000 kg/m^3) have rather high strength for heat-insulators (0.9 – 2.4 N/mm^2) facilitating their transportation, assembly, and operation in furnaces. Heat-insulating refractories have a bulk density comparable to that of known high-temperature thermal insulators, but a significantly lower thermal conductivity: at a temperature of 200°C the thermal conductivity of articles with apparent porosity from 400 to 1000 kg/m^3 ranges in the limits of 0.09 – 0.23 W/(m · K), for fibrous heat-insulating materials — 0.12 – 0.15 W/(m · K), for diatomite products — 0.2 – 0.3 W/(m · K), and for chamotte ultralightweight with apparent density 400 kg/m^3 — 0.18 – 0.22 W/(m · K).

In order to put into production the above listed materials, the company management has approved a program of constructing prototype plants in 2004 for the production of the specified heat-insulating products. After testing the prototype products with consumers and creating a demand, the prototype plants will be converted into industrial production lines. [4]

Thixotropic concrete articles. Another advanced technical direction in the practice of industrial furnaces is the application of refractory concretes, which makes it possible to substantially simplify and mechanize the construction process, as well as simplify and reduce the production cost of refractories of a complex configuration without using presses. At present low-cement thixotropic refractory concretes with high spreadability and needing a low water content are gaining wide acceptance.

The technology of producing articles from low-cement concretes implies the hardening of concrete at a lower temperature (800 – 1000°C) and the development of a fine-capillary structure in the material, which lowers its capacity for impregnation by various melts. The combination of the inert corundum filler and the fine-capillary structure produces a higher chemical resistance. Furthermore, the advantages of

TABLE 4

Parameter	Standard for low-cement concrete*				
	ShBT-1	ShBT-2	MKBT	KBT	KShBT
Type of filler	Chamotte		Mullite-corundum	Corundum	Corundum-spinel
Mass content for calcined material, %:					
Al_2O_3, at least	50.0	55.0	80.0	96.0	94.0
MgO, at least	–	–	–	–	3.0
Fe_2O_3, not more than	1.7	1.5	1.5	0.5	1.0
CaO, within limits	1.0 – 2.0	1.0 – 2.0	1.0 – 2.0	1.0 – 2.0	0.5 – 2.0
Open porosity, %, not more than	23	22	22	22	22
Compression strength in dried state, N/mm^2, at least	30	35	35	30	30
Additional linear shrinkage, %, not more, at temperature, °C:					
1400	0.8	–	–	–	–
1450	–	0.8	–	–	–
1500	–	–	1.0	–	–
1600	–	–	–	0.8	0.5
Thermal resistance, number of thermal cycles (1300°C – water), at least	–	–	–	–	35

* Concrete ShBT-1, ShBT-2, MKBT, and KBT are produced according to TU 14-194-221–98 with modification1, concrete KShBT according to a technical agreement between the customer and the producer.

these materials include high strength at different service temperatures and high thermal resistance, since that batch does not contain argillaceous components and low-melting impurities (oxides of iron, titanium, or alkali metals). The molding technology provides for a uniform thickness and a high accuracy of the sizes of the products.

To attain an indefinite storage period and prevent the destruction of thixotropic concrete products when heater in the consumer's service, the Borovichskii Works performs their preliminary firing at a temperature above 1000°C.

The use of concrete products makes it possible to reduce the number of standard sizes required in brickwork, to avoid labor-consuming cutting and adjustment operations (by agreement with the customer grinding of products can be performed at the producer company), and decrease the duration of repair and assembly works. Compared to the traditional chamotte, high-alumina, and other refractories used in certain elements of glass-melting furnaces, thixotropic concrete products have significantly higher physicochemical parameters.

The Borovichskii Works has accumulated a certain experience in cooperation with glass factories in supplying thixotropic concrete refractory products. Such products have been supplied to various enterprises in the Russian Federation and the CIS countries: Borskii, Malovisherskii, Rostovskii, and Chegodoshchenskii Glass Works, Aktis Company, Kamyshinski Glass Container Factory, Gusevskii Crystal Glass Works, Saratovstroisteklo JSC, Gomel'steklo JSC, etc. Thixotropic concretes are used to produce elements of the cooling and working zones of the furnace, burner blocks, trays, large blocks replacing chamotte bottom bars, and many others by customers' orders [5]. Grinding of refractory products is possible by the customer's order.

The Borovichskii Works has developed a technology for low-cement concrete with higher (up to 1.5 times) thermal resistance compared to the existing materials. It is a concrete with a corundum-spinel filler. This concrete was used to produce burner blocks for the Borskii Glass Works. In October 2003 the burner blocks were installed on the 2nd and 4th pairs of burners. The temperature in this zone is 1500°C, and the flame direction is changed every 30 min. At present the state of the burner blocks is satisfactory, their service continues.

The Borovichskii Works together with the Tsentr-Steklo-Gas R&D Company investigated resistance to glass in various types of refractories. The cooperation with the Tsentr-Steklo-Gas Company has substantially expanded the geography of customers and increased the number of glass-melt elements made of low-cement concretes. For instance, Tsentr-Steklo-Gas has designed original refractory feeder parts for glass-forming machines. Feeder channel section, cover plates, gates, and other elements were produced at the Borovichskii Works and delivered to Dmitrov, Ulyanovsk, and Novosibirsk Works, Svet JSC (city of Mozhga), and some other factories in this sector of industry. The specifications of low-cement (thixotropic) concretes are given in Table 4.

Thus, the use of thixotropic concrete products having high service parameters makes it possible to save the cost of construction and assembly works, extend the service life of certain furnace elements (burner stones), and avoid using expensive bacor refractories (furnace feeders).

Periclase-spinel articles. In recent years, a trend of increasingly extensive use of periclase refractories in glass-melter regenerators is observed, which is intended to extend the furnace campaign without stopping it for hot repairs. As a

TABLE 5

Parameter	Refractory PShAM-1	
	requirements of TU 14-194-251–02	actual data
Mass content for calcined material, %:		
MgO, at least	85.00	89.40
Al_2O_3, within limits	4.00 – 8.00	5.88
CaO, not more than	1.50	1.21
SiO_2, not more than	1.00	0.49
Fe_2O_3, not more than	1.00	0.98
ZrO_2, within limits	1.00 – 3.00	1.51
Open porosity, %, not more than	17.00	15.3 – 15.9
Apparent density, g/cm^3, at least	2.90	2.94 – 2.95
Compression strength, N/mm^2, at least	40	76 – 92
Deformation start temperature under loading, °C, at least	1690	1690
Thermal resistance, number of thermal cycles (1300°C – water), at least	7	9 – 11
Thermal conductivity, W/(m · K),* not more than	4.50	3.61
Additional linear shrinkage at 1650°C, %, not more than	0.7	0.3 – 0.4

* Temperature on the hot side 1000°C.

rule, Russian glass producers use domestic. periclase or periclase-chromite refractories. This type of refractory has evident advantages used as regenerator walls and checkerwork has evident advantages compared with other high-temperature refractories (mullite, mullite-corundum, and forsterite) [6].

Since1990s the Borovichskii Works has been developing fire-resistant articles of high-quality periclase materials, primarily for the needs of the metallurgical industrial complex. Later, in 2000 the company started the production of a new generation of periclase-spinel refractories, which are at the level of the best European analogs.

Periclase-spinel refractories are produced from high-quality materials: high-purity sintered periclase with MgO content not less than 97% and melted (previously synthesized in melting) aluminomagnesial spinel with the total content of Al_2O_3 and MgO at least 97%. An additive of aluminomagnesial spinel to periclase refractories decreases their thermal conductivity and TCLE and increases their heat resistance. A characteristic feature of melted spinel $MgAl_2O_4$ is its high resistance to alkali melts, alkali-bearing materials, acids, carbon, and alkali-earth oxides. The introduction of additives (zirconium and titanium oxides) makes it possible to ensure a more thermostable structure in the product [4].

In April 2003 these refractories were placed in the upper row of the 3rd left regenerator chamber of the glass-melting furnace LTF-1 in a scheduled checkerwork replacement. The service conditions are as follows: the temperature of gas in the regenerator in the place of installing the refractory on the inlet side is 1350 – 1450°C, on the outlet side — 600 – 700°C, a temperature shift each 20 min. The service of these refractories continues and their state is satisfactory.

It should be noted that the Saratovstroisteklo JSC has a vast experience (including negative) of using different magnesian refractories (periclase, periclase-chromite, periclase-spinel) from other producers. The service conditions being equal, the merits and drawbacks of refractories used to be revealed in the first months of their service. Therefore, the results of testing the refractory PShAM-1 produced at the Borovichskii Works at the Saratovstroisteklo furnace can be regarded as positive. The physicochemical parameters of periclase-spinel refractory PShAM-1 are shown in Table 5.

To raise the resistance of refractories intended for the upper checkerwork rows of glass-melter regenerators, the Borovichskii Works has developed a periclase-spinel refractory based on melted high-purity periclase with at least 96% MgO and melted aluminomagnesial spinel with the total content of Al_2O_3 and MgO at least 97%. Melted periclase makes it possible to significantly increase the corrosion resistance of the refractory, since melted periclase crystals are significantly larger than sintered crystals, which ensures a significantly smaller number of interfaces through which a corrosion-causing reactant may penetrate into the depth of the refractory. The new material is graded PShAM-2. Similarly to PShAM-1 refractories, spinel in PShAM-2 articles is a second phased significantly raising its thermal resistance, but at the same time it is protected from external effects by the melted periclase matrix.

Physicochemical Parameters of Periclase-Spinel Products PShAM-2

Parameter	Standard for refractory PShAM-2
Mass content for calcined material, %:	
MgO, at least	85.0
Al_2O_3, within limits	6.0 – 10.0
CaO, not more than	2.0
SiO_2, not more than	1.3
Fe_2O_3, not more than	1.3
ZrO_2, within limits	1.0 – 3.0
Open porosity, %, not more than	17
Apparent density, g/cm^3, at least	3.0
Compression strength, N/mm^2, at least	50
Deformation start temperature under loading, °C, at least	1690
Thermal resistance, number of thermal cycles (1300°C – water), at least	10
Thermal conductivity, W/(m · K),* not more than	It not prescribed
Additional linear shrinkage at 1650°C, %, not more than	0.5

* Temperature on the hot side 1000°C.

The Borovichskii Refractory Works has lately put into production a profiled bowl-shaped checker of the chamotte, mullite-corundum, and periclase-spinel compositions. The use of “bowl-shaped” refractories for regenerator checker-

work in glass-melting furnaces makes it possible to significantly reduce the consumption of energy carriers and accelerate the construction of regenerator checkerwork. The active implementation of latest developments is being continued.

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